CATALYTIC ASPECTS OF SYNTHETIC FUELS FROM COAL

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It is appropriate that this symposium honoring Dr. Storch should focus on catalysis, a field in which he made so many contributions and in which he published widely, most recently posthumously in the comprehensive review with Dr. William Wu (1). It was my priviledge to know Henry Storch and to be greatly impressed by his high scientific standards and his creative research accomplishments. One of his greatest contributions was in attracting to the Bureau of Mines and training highly competent scientists and engineers who still constitute a research resource of great present national value and who, in a real sense, are continuing his research efforts.

I am greatly honored to be the recipient of the 1975 Storch Award for advancement of coal chemistry. Until 1968, my work involved primarily petroleum research. This year's award is a further sign of the integration of coal and petroleum chemistry into a single more fundamental field of the science of fossil fuel energy. Also, this award more than usually is a recognition of the contributions of my colleagues, particularly those in the Bureau of Mines Laboratories (now the Energy Research and Development Administration) since this is where recent experimental work was carried out.

The following papers in the symposium deal with specific topics of synthetic fuels and chemicals from coal. It is my priviledge to discuss certain aspects of catalysis research which seem important to draw to your attention. For this purpose, research programs in which I have been involved will be used to illustrate ideas believed to be of catalytic significance including implications for the future.

Coal Liquefaction

Catalysis is vitally needed for the success of each of the four generic coal liquefaction processes--pyrolysis, solvent extraction, direct hydroliquefaction, and indirect synthesis (from $CO + H_2$). Liquids produced by pyrolysis and by solvent extraction require catalytic refining to remove unwanted constituents (sulfur, nitrogen and oxygen) and to upgrade them to the proper boiling point and, if the desired product is gasoline, to provide the suitable octane number quality.

Pyrolysis

An early catalytic coal project concerned the cracking/refining of tar produced by low temperature pyrolysis of coal. It was found that active catalysts suitable for cracking petroleum produced very high coke yields but greatly improved results could be obtained by using

very low activity catalysts. This type of catalyst provided the best balance of reactions for cracking of coal tars, which have a high tendency to coke.

In a similar situation--cracking petroleum residua--the use of a low activity cracking catalyst was found to give the best products distribution including lowest coke. This was developed to a commercial scale--the Houdresid Process (2). In this case, a relatively large amount of steam was used with the reactants to assist in desorbing reactive fragments (3).

Now, it is important to recognize that frequently in the application of catalysis, it is necessary to <u>balance</u> the kinetics of several reactions proceeding simultaneously. For both coal and coal derived liquids, it is desired to carry out molecular cracking and yet to avoid polymerization (especially of asphaltenes) which lead to coke formation, Figure 1a and 1b. Thus, the functional properties of the catalyst must be balanced and conditions of operation, notably temperature, must be adjusted so as to accomplish cracking but avoid coking.

Litol

Another experience in coal catalysis was the development of a catalyst to upgrade the "light oil" produced in conventional high temperature coking of coal. (Incidentally, it is of practical significance that one fifth of all coal mined in the United States is employed in the production of metallurgical coke, vital in the manufacture of steel.) The so called secondary light oil, boiling about the $140 - 300^\circ F$ range, contains, beside benzene, higher aromatic homologs, sulfur containing compounds, especially thiophene, as well as paraffins. For high quality benzene required by the chemical industry, even 0.1 percent paraffins are too much and the sulfur content must be reduced to less than one ppm. In the LITOL process developed at the Houdry Laboratory, light oil and hydrogen are passed at high temperature and pressure over a fixed bed of catalyst. Sulfur compounds are converted to H_2S (C_4H_4S thiophene + $H_2 \longrightarrow C_4H_{10} + H_2S$), paraffins to gases ($C_4H_{16} + H_2 \longrightarrow C_3H_8 + C_4H_{10}$) and some hydrodealkylation occurs ($C_6H_5CH_3 + H_2 \longrightarrow CH_4 + C_6H_6$).

The chemical constituents of a typical change and product are given in Table 1 (4). The benzene product is of 99.94 percent purity or better and contains less than 0.05 ppm CS_2. The kinetics and reaction mechanism sequence for hydrodealkylation as well as process engineering have been described (5).

Concurrent with process development, it was necessary to produce a catalyst with suitable activity selectivity and stability. Stability was a special problem because of the relatively high temperatures used.

As the result of systematic studies of the effect of variables outlined above plus some inventive ideas as how to prevent crystal growth (leading to inactivation), a catalyst was developed having performance life of several years and which is in commercial use internationally (cf. 6).

	MOLES	
	FEED	PRODUCTS
BENZENE	160.6	175.6
TOLUENE	23.7	17.1
XYLENE	6.6	1.4
STYRENE	2.4	
INDENE	1.8	
C_9 + AROMATICS	0.7	
PARAFFINS & OLEFINS	1.1	
THIOPHENE	2.1	
C_1 to C_4		53.7
H_2S		2.1

TABLE 1.   LITOL PROCESS CHEMCIAL BALANCE

The systematic research program measured and co-related prepara-
tional methods with physical, chemical, and catalytic properties.
Preparational variations are:

- major constituents Cr_2O_3, Al_2O_3 and minor, eg., Na_2O, SiO_2
- method of preparation - coprecipitation, dipping
- conditions of drying and calcining - time, temperature,
  atmosphere
- pellet formation

Physical and chemical properties include:

- crystal structure, surface area, pore volume, pore size
  distribution
- pellet strength
- state of surface oxidation and of acidity by oxygen chemi-
  sorption, iodine and base titration

A further variation in control of surface chemistry, and hence of
catalytic properties, is by the addition of compounds added while in
process, sulfur, ammonia, water, halides, etc.

To correlate the effect of preparation variations with catalytic
properties, standardized catalytic tests were carried out, tests
designed to provide diagnostic information. Model compounds tested
individually can be used to determine dehydrogenation properties--
cyclohexane, isomerization-cyclohexene, and dehydrogenation/isomerization
interaction - methyl cyclopentane (7). Test conditions are chosen to
yield less than equilibrium products. These tests can be correlated with
catalyst preparation variables and with physical and chemical tests.

The point to be made is that the "art" of catalysis, important to
success, is to recognize, measure, and control the critical importance
of, for example, drying a gel when enormous structural changes occur
which determine the character of the catalyst just as importantly as
overall composition. Only a few attempts have been made to describe
in a methodical manner techniques in catalyst preparation.

Coal Hydroliquefaction

A comparison of the chemical composition of coal, petroleum, and
gasoline (Table 2) and molecular structure quickly identified from a
chemical viewpoint the changes which are required to transform coal to
petroleum products. In fact, five changes or steps are needed. First,
it is necessary to transform coal into a liquid form, second to remove
inorganic matter (ash), and third to remove S, N, and O heteroatoms
and transform asphaltenes, usually by means of hydrogenation. Fourth,
molecular size must be reduced (cracking) and frequently a fifth step
is needed to increase the octane number of the gasoline produced
(reforming). Bringing coal to a liquid state is relatively rapid,
but the product formed is high in asphaltenes. It is the hydro-
cracking of asphaltenes which is slow. In actual practice some over-
lapping of reactions occurs in a single process step, e.g., partial
cracking and hydrogenation occur during liquefaction. Figure 2, taken

TABLE 2. CHEMICAL COMPOSITION OF SOME COALS AND PETROLEUM

	Anthracite	Medium volatile bit.	High volatile A bit.	High volatile B bit.	Lignite	Petroleum crude	Gasoline	Toluene
C	93.7	88.4	84.5	80.3	72.7	83-87	86	91.3
H	2.4	5.0	5.6	5.5	4.2	11-14	14	8.7
O	2.4	4.1	7.0	11.1	21.3			
N	0.9	1.7	1.6	1.9	1.2	0.2		
S	0.6	0.8	1.3	1.2	0.6	1.0		
H/C atom ratio	0.31	0.67	0.79	0.82	0.69	1.76	1.94	1.14

Coal analysis on moisture- and ash-free basis. Ash content of coal 3 to 15 percent.

C-fraction aromatic = 0.7. Aromatic rings per cluster--not over 3. H_{arom}/H_{aliph} = 0.23.

H/C atom ratio of petroleum residua: asphaltenes 1.18, resin 1.47, oil 1.67.

from a review (8) which emphasizes novel catalysts, also depicts how three types of liquefaction processes accomplish the required changes. Catalysts used by the Germans (9) as well as more modern petroleum catalysts are also specified.

Mechanism of Hydroliquefaction

An overall mechanism of catalytic hydroliquefaction of coal (10) which has much support for many catalyst systems views the primary step to be transformation of coal to asphaltenes. This can occur principally as a thermal reaction. The highly reactive fragments alternatively can polymerize or they can be hydrogenated to stable products if suitable catalytic circumstances are provided (Figure 3). The catalyst must be able to provide rapidly activated hydrogen to the fragments. Of course, additional transformations can occur on the catalyst surface, such as isomerization and/or cracking. According to this scheme, the amount of benzene insolubles, asphaltene and oil in the product depend upon the relative rates of splitting, hydrogenation-stabilization of fragments, and polymerization of fragments. The product distribution should correspondingly depend upon the presence of splitting catalysts, hydrogenation catalysts and high pressure hydrogen. Catalysts have been examined from this viewpoint as a means of determining how they function (10). The importance of knowing the actual at least major pathway is that it leads to ideas for improvements of key steps and control of proper transport, hydrogen accessibility, etc. The above pathway--thermal cracking and subsequent catalytic transformation-- is consistent with the practice of using high hydrogen pressures (to provide for hydrogen availability) and avoidance of too high temperatures where the generation of reactive fragments would exceed the capability of the catalyst to handle them, especially as the rate of undesirable polymerization increases at a higher power.

Synthoil

The growing capability to hydrotreat petroleum over fixed-bed catalysts, led to my suggestion that mixtures of coal in recycle oil could be directly liquefied over $Co-Mo-Al_2O_3$ type catalysts. In the first experiments, to the surprise of some, runs of many hours were achieved without plugging the reactor and with promising conversion levels. Later concepts by others for operation with a reactor geometry and hydrogen flow rate so as to have gaseous turbulent flow demonstrated further advantages in catalyst stability and reactivity leading to the development of the Bureau of Mines Synthoil Process. A pilot unit capable of processing about eight T/D is being constructed. The development of the Synthoil process has been carried out vigorously by Aktar and Yavorsky (11) and their associates. They have described in detail the effect of process variables and provided an insight as to the reactions from the chemical/structural nature of the products.

As far as the catalyst is concerned, some variations in composition and physical structure have been established, although it is fair to say that much remains to be established and there appear to be real opportunities for improvements.

Catalysis for the Integral Gasification
Hydrocarbon Synthesis (IGHS)

The objective of the transformation of coal into hydrocarbons can be symbolized from a chemical viewpoint by the reaction

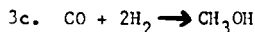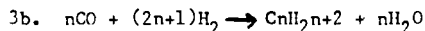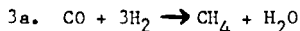1. $2C + 2H_2O \longrightarrow CH_4 + CO_2$.
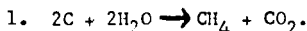
This reaction is balanced stoichiometrically and nearly so calorimetrically. However, as is well known, for the steam-carbon reaction to occur at sufficient speed to be of commercial interest requires a temperature of about $900°C$. This high temperature results in primarily $H_2 + CO$ as products since hydrocarbons are not sufficiently stable.

2. $C + H_2O \longrightarrow H_2 + CO$
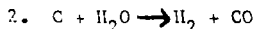
Reaction (2) is highly endothermic.

Three reactions between CO and H_2 which are of interest occur below about $500°C$

3a. $CO + 3H_2 \longrightarrow CH_4 + H_2O$

3b. $nCO + (2n+1)H_2 \longrightarrow CnH_2n+2 + nH_2O$

3c. $CO + 2H_2 \longrightarrow CH_3OH$

These reactions are all exothermic.

If the steam-carbon reaction (1) could be accelerated so as to proceed sufficiently rapidly at $500°C$, then products shown in reaction (3) could be produced simultaneously with improved thermal efficiency and also with lower equipment cost. Thus, there is a great opportunity for development of catalytic systems to speed up the steam-carbon reaction (12), (13).
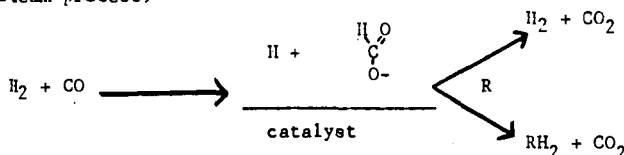
In our work on the Synthane coal gasification, the integrated gasification-hydrocarbon synthesis (IGHS) was accomplished to a substantial extent. This was achieved in part by the mechanical arrangement by using a fluid bed having two zones, the top or exit zone operating at about $1400°F$ as shown in Figure 4 (14). As an example, product gas from Illinois #6 coal on a mole percent basis is 17 CH_4, 31 H_2, 20 CO, and 32 CO_2. On a CO_2-free basis, the methane is 26 percent and is more than half the ultimate methane in the gas following methanation.

It is also believed that the mineral matter in the coal (Fe, Na, and Ca) plays a significant role in hydrocarbon synthesis. Haynes and Forney have shown the acceleration of gasification by adding inorganic salts (15). The rapid rate of gasification of lignite is at least partially attributable to its high alkali content. Possibly recirculation of high alkali ash will be a useful catalytic procedure.

An important objective should be to carry out coal gasification/hydrocarbon synthesis as a single integrated operation. While methane is desirable, it should also be possible to produce higher hydrocarbons (transportation of ethane and propane by pipeline is more economical than methane). It should also be possible to produce methanol and/or aromatic hydrocarbons integrated with coal gasification. The advantages

of manufacturing methane/methanol as co-products was previously pointed out (16).

An additional interesting point is that base catalysts are effective in the steam-carbon reaction. The petroleum industry rarely employs base catalysts. Base catalysts have many unusual characteristics, for instance, the nature of reactant/catalyst complex. Some evidence points to a formate ion intermediate, which results in either $H_2 + CO_2$ or alternatively to a hydrogenated product RH_2 if a hydrogen acceptor, R, is present. (CO-steam process)

$$H_2 + CO \longrightarrow \underbrace{\begin{array}{c} H + \begin{array}{c} O \\ C \\ O- \end{array} \end{array}}_{\text{catalyst}} \begin{array}{c} \nearrow H_2 + CO_2 \\ R \\ \searrow RH_2 + CO_2 \end{array}$$

Perhaps even more significant for coal chemistry is the concept that the catalyst is mobile. Normally in catalytic reactions, the reactants move to an active catalyst site. However, catalytic substances (alkali) having surface mobility or indeed having volatility can operate by moving the catalyst to solid char reactant. In a broad sense, this is an example of the unusual dynamic nature of catalysts proposed some years ago (17).

Future

There is a major recent national commitment to manufacture synthetic fuels from coal on a massive scale and in what must be regarded as essentially the immediate future. This commitment recognizes that a major research and development effort is vitally needed to accomplish the installation of processes which are of improved efficiency and cost. Federal funding is being provided and growing academic and industrial support. Several workshop meetings (18-22) have set forth the technical background, objectives, and priorities. Prominent in research recommendations are all aspects of catalysis. The importance in carrying out systematic diagnostic catalytic tests to follow variations in catalyst preparation seems to need more emphasis in comparison to the approach of fundamental knowledge of the physics of surfaces. At this stage of development, the reaction mechanism, including transport phenomenon, needs clarification in order to provide the basis for improving key slow steps. Also, new ideas are needed and must be tested in the areas of photo, bio or coordination, basic and mobile catalysts. Based on the advances made in applied catalysis in the last several decades in fuel chemistry, especially in the petroleum and petrochemical industry, it can be expected with confidence that major new catalytic developments will provide the technology for a highly effective synthetic fuels from coal industry.
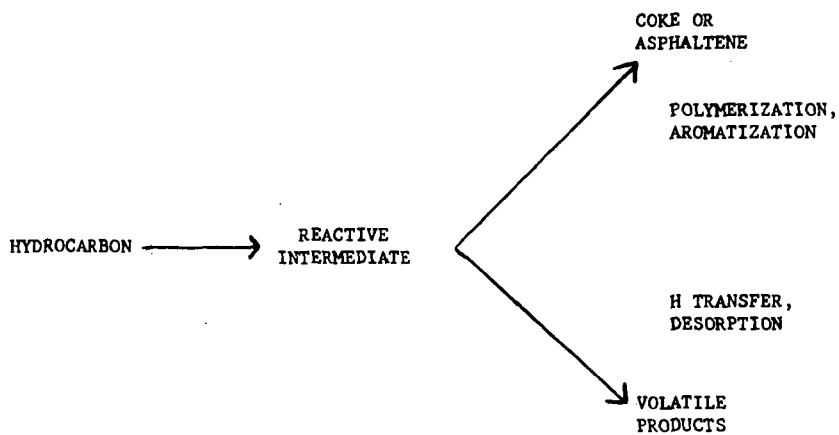
COKE OR
ASPHALTENE

POLYMERIZATION,
AROMATIZATION

HYDROCARBON ⟶ REACTIVE
INTERMEDIATE

H TRANSFER,
DESORPTION

VOLATILE
PRODUCTS

FIGURE 1a. ALTERNATE PATHS, REACTIONS CONTROLLING RELATIVE RATES
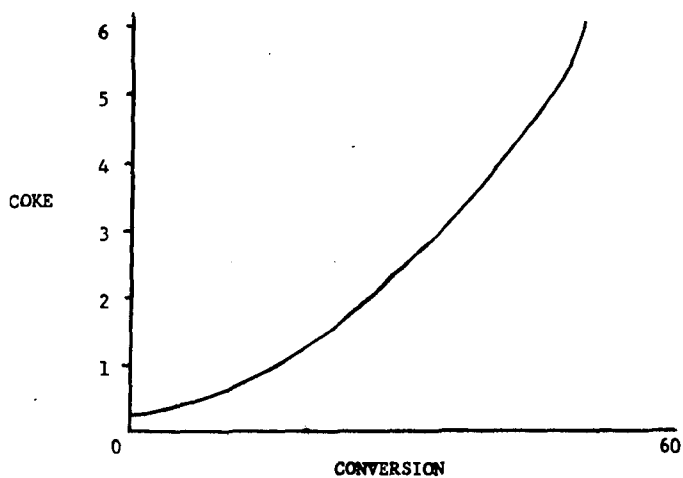
FIGURE 1b. INCREASE IN COKE IN CAT CRACKING

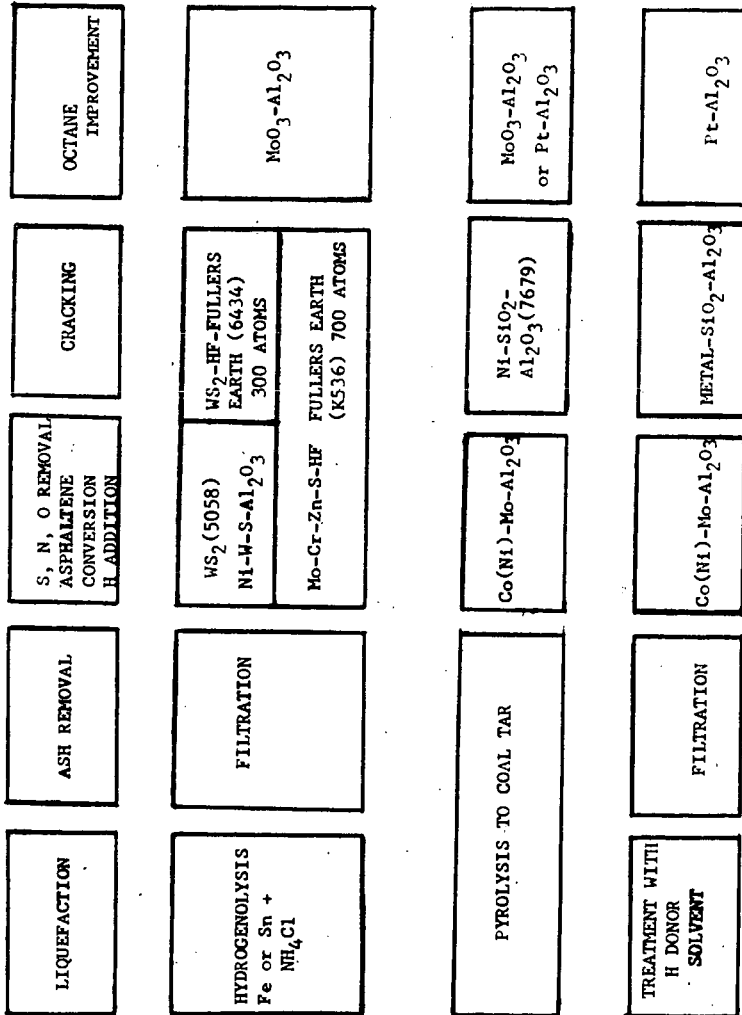| LIQUEFACTION	ASH REMOVAL	S, N, O REMOVAL ASPHALTENE CONVERSION H ADDITION	CRACKING	OCTANE IMPROVEMENT

HYDROGENOLYSIS Fe or Sn + NH_4Cl	FILTRATION	WS_2(5058) Ni-W-S-Al_2O_3 / Mo-Cr-Zn-S-HF	WS_2-HF-FULLERS EARTH (6434) 300 ATOMS / FULLERS EARTH (K536) 700 ATOMS	MoO_3-Al_2O_3

PYROLYSIS TO COAL TAR	Co(Ni)-Mo-Al_2O_3	Ni-SiO_2-Al_2O_3(7679)	MoO_3-Al_2O_3 or Pt-Al_2O_3

TREATMENT WITH H DONOR SOLVENT	FILTRATION	Co(Ni)-Mo-Al_2O_3	METAL-SiO_2-Al_2O_3	Pt-Al_2O_3

FIGURE 2. CONVERSION OF COAL TO GASOLINE

COAL

ASPHALTENE

GAS   REACTIVE
             FRAGMENT

(ACID
CATALYST)   (HYDROGENATION)

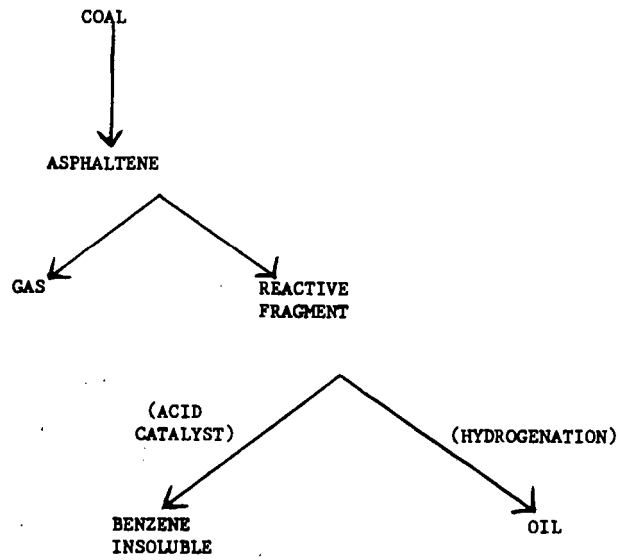BENZENE   OIL
INSOLUBLE
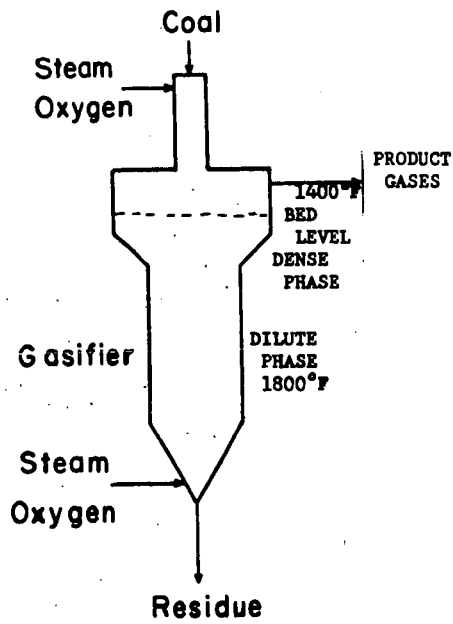
FIGURE 3. MECHANISM OF COAL CONVERSION

FIGURE 4.
SYNTHANE GASIFIER TEMPERATURE PATTERN

13

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